PATENT SPECIFICATION

DRAWINGS ATTACHED

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Int. Cl.:—C 23 c//H 01 c

COMPLETE SPECIFICATION

Improvements in or relating to Film Resistors

We, WESTERN ELECTRIC COMPANY, INCORPORATED, of 195 Broadway, New York City, New York State, United States of America, a Corporation of the State of New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to film resistors, and methods of fabrication thereof.

In recent years, the miniaturization of components and circuitry has been a major development activity in the electronics industry. Particular emphasis has been placed upon the development of a thin film material, suitable for resistor purposes, which evidences the combined properties of high specific resistivity, a low temperature coefficient of resistance and high thermal stability.

Among the more promising materials developed thus far have been sputtered films of tantalum which typically evidence resistivity values of 250 ± 50 micro ohm—cm, sheet resistance values of the order of 100 ohms/square, temperature coefficient of resistance of approximately ± 100 ppm/°C. and thermal stabilities of ± 2% change in resistance after 1000 hours at 100°C. Although such tantalum components are widely used and satisfactory for most device purposes, the need has developed for a technique of fabricating a resistor film material which evidences appreciably higher resistivity and stability than heretofore attained while maintaining effective temperature coefficients.

In accordance with one aspect of this invention there is provided a method of fabricating a deposited film resistor, in which deposition of tantalum on to a substrate occurs in an atmosphere containing oxygen such that the tantalum reacts with the oxygen to form an amorphous film of tantalum metal and tantalum pentoxide.

In accordance with another aspect of the invention there is provided a deposited film resistor comprising an amorphous film of tantalum and tantalum pentoxide deposited on a substrate, which, fabricated by the method described herein results in a product evidencing specific resistivities of 1000 micro ohm—cm and higher, sheet resistance values of 1000 ohms/square and temperature coefficients of resistance within the range of −200 to −300 ppm/°C. These desirable properties are achieved with an unusual increase in thermal stability, amounting to less than 0.1 per cent change in resistance after 1000 hours at 150°C. Furthermore, in isolated instances where high resistivities are of major importance, as in the case of carbon composition resistors, films with appreciably higher resistivities are feasible.

The invention will be more particularly described with reference to the accompanying drawings in which:

FIG. 1 is a front elevational view, partly in section, of an apparatus suitable for use in producing a film by reactive sputtering.

FIG. 2 is a graphical representation on coordinates of specific resistivity in micro ohm—cm against the oxygen flow rate per gram sputtered tantalum measured in micron cubic feet per gram (micron meaning pressure expressed in microns of mercury) showing the variations of resistivity at 25°C. of 500 Å tantalum films sputtered with varying oxygen flow rates with a total argon plus oxygen pressure of 20 to 25×10^{-3} torr with subsequent anodization at 25 volts D.C. and thermal preaging in air at 250°C. for 5 hours;

FIG. 3 is a graphical representation on coordinates of temperature coefficient of resistance in parts per million per degree centigrade against the oxygen flow rate per

[Price

gram sputtered tantalum measured in micron cubic feet per gram showing variations in temperature coefficient of resistance at 25°C. of 500 Å tantalum films sputtered with varying oxygen flow rates with a total argon plus oxygen pressure of 20 to 25×10^{-3} torr with subsequent anodization at 25 volts and thermal preaging in air at 250°C. for 5 hours; and

FIG. 4 is a graphical representation on coordinates of change in resistance (per cent) at 1000 hours against the oxygen flow rate per gram sputtered tantalum showing variations in resistance after 1000 hours at 150°C.

With reference more particularly to FIG. 1, there is shown an apparatus suitable for depositing films by reactive sputtering. Shown in FIG. 1 is a vacuum chamber 11 in which are disposed cathode 12 and anode 13. Cathode 12 may be composed of tantalum or, alternatively, may serve as the base for the tantalum which latter may be in the form of a coating, foil or other suitable physical form.

A source of electrical potential 14 is shown connected between cathode 12 and anode 13. Platform 15 is employed as a positioning support for substrate 16 upon which the sputtered film is to be deposited. Mask 17 is placed on substrate 16 to restrict the deposition to this area.

The present method is conveniently described in detail by reference to an illustrative example in which tantalum is employed as cathode 12 in the apparatus shown in FIG. 1.

Preferred substrate materials are glasses or glazed ceramics. These materials meet the requirements of heat resistance and non-conductivity essential for substrates utilized in reactive sputtering techniques.

Substrate 16 is first vigorously cleaned. Conventional cleaning agents are suitable, the choice of a specific one being dependent upon the composition of the substrate itself. For example, where the substrate consists of glass, boiling in aqua regia or hydrogen peroxide is a convenient method for cleaning the surface.

Substrate 16 is placed upon platform 15, as shown in FIG. 1, and mask 17 is then suitably positioned. Platform 15 and mask 17 may be fabricated from any refractory material. However, it may be convenient to use a metal, such as aluminium, for ease in fabricating mask 17. To obtain sharply defined deposits, it is necessary to have mask 17 bearing against substrate 16 under externally applied pressure.

In order to obtain the desired properties and to maintain close control of the process it is essential to initially evacuate the system to 10^{-6} torr, thereby assuring a sufficiently low level of background gas. Next, oxygen is admitted at a dynamic pressure and after attaining equilibrium argon is admitted.

Increasing the inert gas pressure and thereby reducing the vacuum within chamber 11 increases the rate at which the tantalum being sputtered is removed from the cathode and thus increases the rate of deposition. The maximum pressure is usually dictated by power supply limitations since increasing the pressure also increases the current flow between cathode 12 and anode 13. A practical upper limit in this respect is 25×10^{-3} torr for a sputtering voltage of 4000 volts although it may be varied depending upon the size of the cathode and sputtering rate. The ultimate maximum pressure is that at which the sputtering can be reasonably continued within the prescribed tolerances. It follows, from the discussion above, that the minimum pressure is determined by the lowest deposition rate which can be economically tolerated. After the requisite pressure is attained, cathode 12 is made electrically negative with respect to anode 13.

The practical minimum voltage necessary to produce sputtering is 2000 volts. Increasing the potential difference between anode 13 and cathode 12 has the same effect as increasing the pressure, that of increasing both the rate of deposition and the current flow. Accordingly, the maximum voltage is dictated by consideration of the same factors controlling the maximum pressure.

The spacing between anode and cathode is not critical. However, the minimum separation is that required to produce a glow discharge which must be present for sputtering to occur. Many dark striations are well known and have been given names, as for example, Crooke's Dark Space (See Joos, "Theoretical Physics", Hafner, New York, 1950, page 435 et seq.). For the best efficiency during the sputtering step, substrate 16 should be positioned immediately without the Crooke's Dark Space on the side closest to the anode 13. Location of substrate 16 closer to cathode 12 results in a deposit of poorer quality. Locating substrate 16 further from cathode 12 results in the impingement on the substrate by a smaller fraction of the total metal sputtered, thereby increasing the time necessary to produce a deposit of given thickness.

It should be noted that the location of Crooke's Dark Space changes with variations in the pressure, it moving closer to the cathode with increasing pressure. As the substrate is moved closer to the cathode it tends to act as an obstacle in the path of gas ions which are bombarding the cathode. Accordingly, the pressure should be maintained sufficiently low so that Crooke's Dark Space is located beyond the point at which a substrate would cause shielding of the cathode.

The balancing of these various factors of voltage, pressure and relative positions of the cathode, anode and substrate to obtain a high quality deposit is well known in the sputtering art.

With reference now more particularly to the example under discussion, by employing a suitable voltage, pressure and spacing of the various elements within the vacuum chamber, an amorphous film of tantalum and tantalum pentoxide is deposited in a configuration determined by mask 17. The sputtering is conducted for a period of time calculated to produce the desired thickness.

The minimum thickness of the film deposited upon the substrate is 400 Angstroms. There is no maximum limit on this thickness although little advantage is gained by an increase beyond 2000 Angstroms.

FIG. 2 is a graphical representation showing the specific resistivity in micro ohm—cm at 25°C. of tantalum films which are 500 Angstroms thick sputtered with a total pressure of 20 to 25×10^{-3} torr of argon plus oxygen plotted as a function of the flow rate of oxygen per gram of sputtered tantalum. Each of the films so prepared was anodized at 25 volts and thermally preaged in air at 250°C. for 5 hours subsequent to sputtering. Two sets of data are presented in order to show variations due to the pumping system employed during sputtering. The films in series A were sputtered using a 25 litre/second diffusion pump while those in series B were sputtered using a 300 litre/second diffusion pump.

As is noted from the graph it is possible to obtain film resistors having specific resistivities ranging from at least 250 micro—ohm cm to values of 100,000 micro—ohm cm, such properties not being heretofore attained in thin film resistors.

An analysis of FIG. 3 which shows the temperature coefficient plotted against flow rate of oxygen per gram of sputtered tantalum for the same group of resistors as represented by the data in FIG. 2 indicates that the rise in resistivity, above anticipated values, is accompanied by a decrease in the temperature coefficient of resistivity to values within the range of -200 to -600 ppm/°C.

The use of oxygen flow rates measured in micron cubic feet per gram of sputtered tantalum within the range of 100—10,000 result in resistivities and temperature coefficients within the desired ranges. Although satisfactory resistors may be obtained when utilizing flow rates less than 100 micron cubic feet per gram a lower limit has been set for practical purposes. The upper limit of 10,000 micron cubic feet per gram is likewise not absolute and flow rates appreciably beyond this level may be employed without causing any deleterious results.

In FIG. 4 there is shown a graphical representation of life test data obtained for the series B resistors which were maintained at 150°C. for 1000 hours. The thermal life test data indicates that enhanced stability is obtained at increasing oxygen flow rates with the trend reversing slightly at flow rates of 4000 micron cubic feet per gram. For the purpose of the present method pure oxygen (having a plurality of 99.99+ per cent) is required.

With reference once again to the example under discussion, the substrate is maintained at temperatures within the range of 100 to 400°C. during the reactive sputtering process. Temperatures below 100°C. result in poor adherence of the film to the substrate due to outgassing of the substrate, whereas temperatures appreciably beyond 400°C. adversely affect stability.

Following the deposition technique, the resultant film which is composed of an amorphous mixture of tantalum and tantalum pentoxide is anodized for the purpose of adjusting the value of resistance to a desired level, such technique disclosed in Patent Specification No. 896071.

Next, the anodized films are heated in the presence of air at temperatures within the range of 250—400°C. for a time period within the range of 1 to 5 hours, thereby stabilizing said films.

An example of the present invention is described in detail below. This example and the illustration described above are included merely to aid in the understanding of the invention.

EXAMPLE

This example describes the fabrication of a tantalum film resistor.

A sputtering apparatus similar to that shown in FIG. 1 was used to produce an amorphous film of tantalum and tantalum pentoxide. The cathode consisted of a circular tantalum disk 250 mils thick and 5 inches in diameter with less than 100 ppm interstitial impurities. In the apparatus actually employed, the anode was earthed, the potential difference being obtained by making the cathode negative with respect to earth.

A glass microscope slide, 1/2 inch in width and 3 inches in length was used as a substrate. Gold terminals, 3/8 inch by 1/4 inch were silk screened on each longitudinal side of the substrate. The gold terminals were fired at 500°C. and had a final resistance of 0.1 ohm per square. The terminated slides were then cleaned using the following procedure. The slides were first washed in a detergent, to remove large particles of dirt and grease, and vigorously washed in tap water for several minutes, followed by a distilled water rinse.

The vacuum chamber was evacuated by means of a roughing pump and an oil diffusion pump to a pressure of 1×10^{-6} torr of mercury after a time period within the range of 1 to 2 hours. Next, the substrate was heated to a temperature of 400°C. After obtaining such temperature, oxygen was admitted into the chamber at a dynamic pressure and

after obtaining equilibrium argon was admitted into the chamber at a pressure of 25×10^{-3} torr. During the sputtering reaction the flow rate of the oxygen was maintained at 1500 micron cubic feet per gram of sputtered tantalum.

The anode and cathode were spaced 2.5 inches apart, the clean substrate being placed therebetween at a position immediately without Crooke's Dark Space. The substrate was maintained at a temperature of 400°C. during the sputtering reaction and a D.C. voltage of 4000 volts was applied across the cathode and anode. In order to establish equilibrium when first initiating the sputtering, it was found helpful to sputter on a shield for 30 minutes, thereby assuring reproducible results. Sputtering was conducted for 5 minutes, producing a layer of 500 Angstroms of an amorphous film of tantalum and tantalum pentoxide. Electrical measurements were made at each stage of treatment of the resistor.

Next, the sputtered film was anodized at 25 volts D.C. utilizing an electrolyte consisting of an aqueous nitric acid solution, .05 per cent by weight. The anodized resistor was then thermally preaged by heating in air at 250°C. for 5 hours.

WHAT WE CLAIM IS:—

1. A method of fabricating a deposited film resistor, in which deposition of tantalum onto a substrate occurs in an atmosphere containing oxygen such that the tantalum reacts with the oxygen to form an amorphous film of tantalum and tantalum pentoxide.

2. A method according to claim 1, in which the substrate is maintained at a temperature within the range of 100° to 400°C.

3. A method according to claim 1 or 2, in which the flow rate of oxygen in the atmosphere is within the range of 100 to 10,000 micron cubic feet per gram of tantalum deposited.

4. A method according to any one of claims 1 to 3, in which the said film is thermally preaged by heating in air.

5. A method according to claim 4, in which the said film is heated to a temperature within the range of 250° to 400°C. for a time period within the range of 1 to 5 hours.

6. The method according to any one of claims 1 to 5, in which the said film is anodized in order to adjust the resistance thereof.

7. A method according to any one of claims 1 to 6, in which formation of the said film is by reactive sputtering.

8. A method according to claim 7, as appended to claim 6, in which deposition of the said film is conducted at a temperature of 400°C. with a flow rate of oxygen of 1500 micron cubic feet per gram of tantalum sputtered, anodizing said film, and heating said anodized film in air at a temperature of 250°C for a time period of 5 hours.

9. A method according to any one of claims 1 to 8, in which the minimum thickness of the said film is 400 Å.

10. A deposited film resistor comprising an amorphous film of tantalum and tantalum pentoxide deposited on a substrate.

11. A method of fabricating a deposited film resistor substantially as herein described with reference to the example.

12. A deposited film resistor fabricated by the method of any one of claims 1 to 9, or claim 11.

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Sheets 1 & 2

FIG. 1

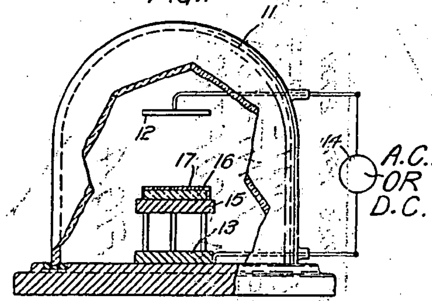

FIG. 2

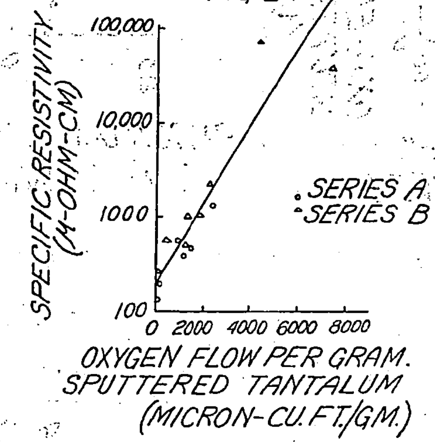

FIG. 3

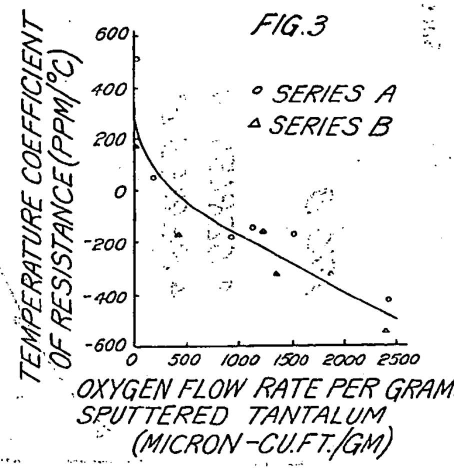

FIG. 4

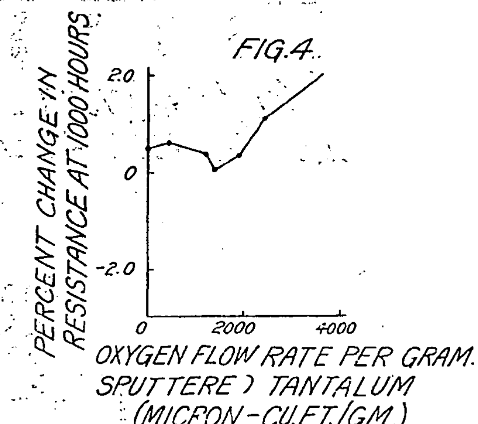

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FIG.3

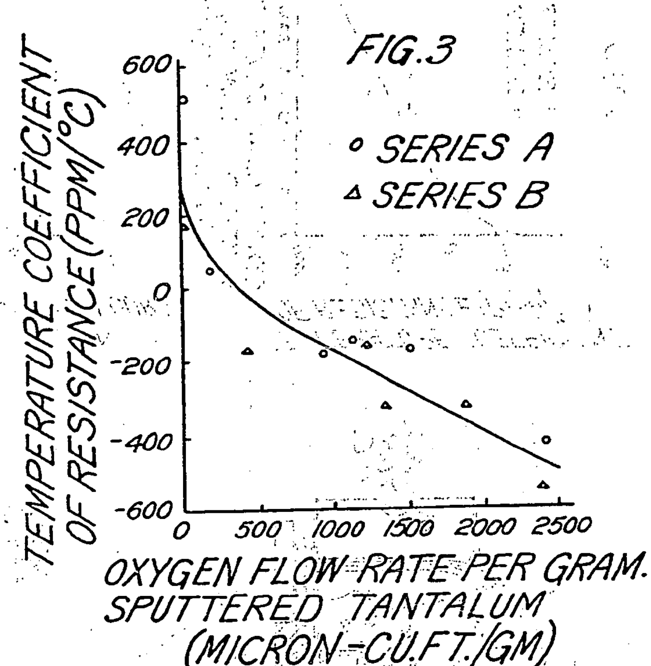


FIG.4

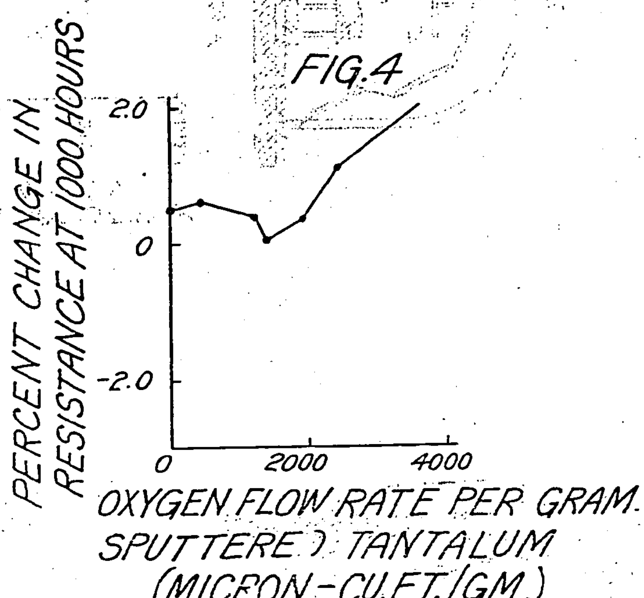
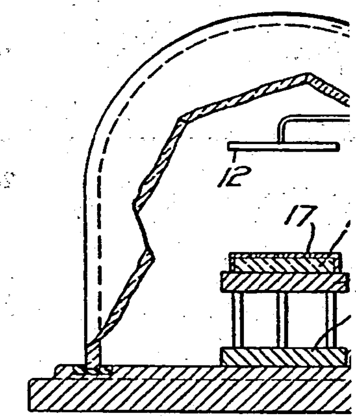


FIG. 1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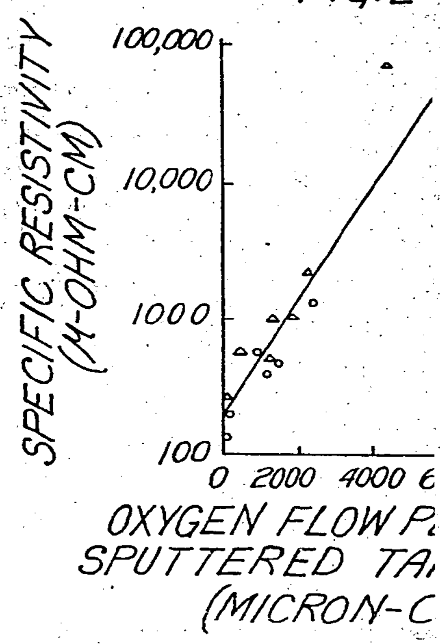
17

FIG. 2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